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| (54) Title: AROMATIC POLYCARBONATE RESIN COMPOSITION FOR MOLDING (57) Abstract A thermoplastic resin composition contains, based on 100 parts by weight of the composition, from 65 to 85 parts by weight of one or more aromatic polycarbonate resins, from 10 to 50 parts by weight of a rubber modified graft copolymer, comprising a discontinuous elastomeric phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase, and from 1 to 15 parts by weight of a mineral filler having a mean largest characteristic dimension of from 0.1 micrometer to 30 micrometers. | | |

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AROMATIC POLYCARBONATE RESIN COMPOSITION FOR MOLDING

This application claims rights of priority from U.S. Provisional Patent Application Serial No. 60/046,568, filed May 15, 1997, which is hereby incorporated by reference.

FIELD OF THE INVENTION

The invention relates to blends of a polycarbonate resin and a rubber modified graft copolymer.

BRIEF DESCRIPTION OF THE RELATED ART

Blends of a polycarbonate resin and a rubber modified graft copolymer and mineral fillers are known, see for example, coassigned U.S. Patent No. 5,162,419, which discloses objects formed by injection molding compositions comprising a polycarbonate resin, a graft copolymer, a copolymer and talc, as well as U.S. Patent No. 5,091,461, which discloses polymeric molding compositions comprising an amorphous polymer matrix and an inorganic filler that are said to exhibit reduced coefficient of expansion, high dart impact resistance and good heat resistance.

There remains an interest in developing filled polycarbonate resin/rubber modified graft copolymer blends that exhibit further improvement in performance, such as for example, higher heat distortion temperature, improved flow, improved low temperature impact properties and improved dimensional stability.

SUMMARY OF THE INVENTION

The thermoplastic resin composition of the present invention comprises, based on 100 parts by weight of the composition:

- (a) from 65 to 85 parts by weight of one or more aromatic polycarbonate resins,
- (b) from 10 to 50 parts by weight of a rubber modified graft copolymer, comprising a discontinuous elastomeric phase dispersed in a continuous rigid thermoplastic phase; wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase, and
- (c) from 1 to 15 parts by weight of a particulate mineral filler having a mean largest characteristic dimension of from 0.1 micrometer to 30 micrometers.

The composition of the present invention exhibits unexpectedly improved dimensional stability, improved thermal performance, improved retention of impact resistance, particularly at low temperatures, and improved flow properties.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 are photomicrographs of a section of a molded article of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

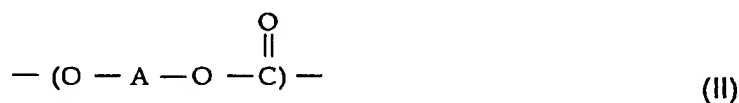
In a preferred embodiment, the thermoplastic resin composition of the present invention comprises, based on 100 pbw of the composition, from 70 to 80 parts by weight ("pbw") of the aromatic polycarbonate resin, from 10 to 24 pbw of the rubber modified graft copolymer, from 6 to 10 pbw of the talc.

Aromatic polycarbonate resins suitable for use as the aromatic polycarbonate resin component of the thermoplastic resin composition of the present invention are known compounds whose preparation and properties have been described, see, generally, U.S. Patent Nos. 3,169,121, 4,487,896 and 5,411,999, the respective disclosures of which are each incorporated herein by reference.

In a preferred embodiment, the aromatic polycarbonate resin component of the present invention is the reaction product of a dihydric phenol according to the structural formula (I):



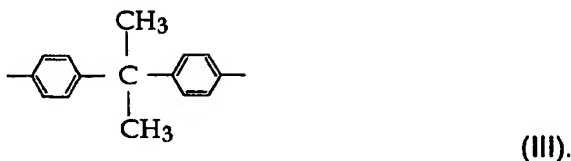
wherein A is a divalent aromatic radical, with a carbonate precursor and contains structural units according to the formula (II):



wherein A is defined as above.

As used herein, the term "divalent aromatic radical" includes those divalent radicals containing a single aromatic ring such as phenylene, those divalent radicals containing a condensed aromatic ring system such as, for example, naphthylene, those divalent radicals containing two or more aromatic rings joined by non-aromatic linkages, such as for example, an alkylene, alkylidene or sulfonyl group, any of which may be substituted at one or more sites on the aromatic ring with, for example, a halo group or (C₁-C₆)alkyl group. As used herein to modify an organic substituent group, the notation "(C_x-C_y)", wherein x and y are each integers, means that the organic substituent group contains from x carbon atoms to y carbon atoms per group.

In a preferred embodiment, A is a divalent aromatic radical according to the formula (III):



Suitable dihydric phenols include, for example, one or more of 2, 2-bis-(4-hydroxyphenyl) propane ("bisphenol A"), 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, bis(4-hydroxyphenyl) methane, 4,4-bis(4-

hydroxyphenyl)heptane, 3,5,3',5'-tetrachloro-4,4'-dihydro-xyphenyl) propane, 2,6-dihydroxy naphthalene, hydroquinone, 2,4'-dihydroxyphenyl sulfone. In a highly preferred embodiment, the dihydric phenol is bisphenol A.

The carbonate precursor is one or more of a carbonyl halide, a carbonate ester or a haloformate. Suitable carbonyl halides include, for example, carbonyl bromide and carbonyl chloride. Suitable carbonate esters include, such as for example, diphenyl carbonate, dichlorophenyl carbonate, dinaphthyl carbonate, phenyl tolyl carbonate and ditolyl carbonate. Suitable haloformates include, for example, bishaloformates of a dihydric phenols, such as, for example, hydroquinone, or glycols, such as, for example, ethylene glycol, neopentyl glycol. In a highly preferred embodiment, the carbonate precursor is carbonyl chloride.

Suitable aromatic polycarbonate resins include linear aromatic polycarbonate resins, branched aromatic polycarbonate resins. Suitable linear aromatic polycarbonates resins include, e.g., bisphenol A polycarbonate resin. Suitable branched polycarbonates are known and are made by reacting a polyfunctional aromatic compound with a dihydric phenol and a carbonate precursor to form a branched polymer, see generally, U. S. Patent Nos. 3,544,514, 3,635,895 and 4,001,184, the respective disclosures of which are incorporated herein by reference. The polyfunctional compounds are generally aromatic and contain at least three functional groups which are carboxyl, carboxylic anhydrides, phenols, haloformates or mixtures thereof, such as, for example, 1,1,1-tri(4-hydroxyphenyl)ethane, 1,3,5,-trihydroxy-benzene, trimellitic anhydride, trimellitic acid, trimellityl trichloride, 4-chloroformyl phthalic anhydride, pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, benzophenonetetracarboxylic acid, benzophenone-tetracarboxylic dianhydride. The preferred polyfunctional

aromatic compounds are 1,1,1-tri(4-hydroxyphenyl)ethane, trimellitic anhydride or trimellitic acid or their haloformate derivatives.

In a preferred embodiment, the polycarbonate resin component of the present invention is a linear polycarbonate resin derived from bisphenol A and phosgene.

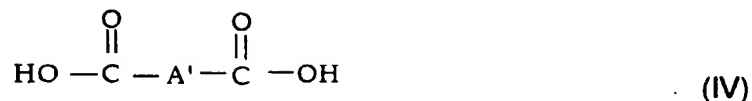
In a preferred embodiment, the weight average molecular weight of the polycarbonate resin is from about 10,000 to more than 200,000 g/mol, as determined by gel permeation chromatography relative to polystyrene. Such resin typically exhibits an intrinsic viscosity of about 0.3 to about 1.5 deciliters per gram in methylene chloride at 25°C. Mixtures of polycarbonate resins of different molecular weights are also useful.

Polycarbonate resins are made by known methods, such as, for example, interfacial polymerization, transesterification, solution polymerization or melt polymerization.

Copolyester-carbonate resins suitable for use as component (c) of the thermoplastic resin composition of the present invention are known compounds whose preparation and properties have been described, see, generally, U.S. Patent Nos. 3,169,121, 4,430,484 and 4,487,896, the respective disclosures of which are each incorporated herein by reference.

Copolyester-carbonate resins comprise linear or randomly branched polymers that contain recurring carbonate groups, carboxylate groups and aromatic carbocyclic groups in the polymer chain, in which at least some of the carbonate groups are bonded directly to the ring carbon atoms of the aromatic carbocyclic groups.

In a preferred embodiment, the copolyester-carbonate resin component of the present invention is derived from a carbonate precursor, at least one dihydric phenol and at least one dicarboxylic acid or dicarboxylic acid equivalent. In a preferred embodiment, the dicarboxylic acid is one according to the formula (IV):



wherein A' is alkylene, alkylidene, cycloaliphatic or aromatic and is preferably a non-substituted phenylene radical or a substituted phenylene radical that is substituted at one or more sites on the aromatic ring, wherein each of such substituent groups is independently (C₁-C₆) alkyl, and the copolyester carbonate resin comprises first structural units according to formula (II) above and second structural units according to formula (V):



wherein A' is defined as above.

Suitable carbonate precursors and dihydric phenols are those disclosed above.

Suitable dicarboxylic acids, include, for example, phthalic acid, isophthalic acid, terephthalic acid, dimethyl terephthalic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dimethyl malonic acid, 1,12-dodecanoic acid, *cis*-1,4-cyclohexane dicarboxylic acid, *trans*-1,4-cyclohexane dicarboxylic acid, 4,4'-bisbenzoic acid, naphthalene-2,6-dicarboxylic acid. Suitable dicarboxylic acid equivalents include, for example, anhydride, ester or halide derivatives of the above disclosed dicarboxylic acids, such as, for example, phthalic anhydride, dimethyl terephthalate, succinyl chloride.

In a preferred embodiment, the dicarboxylic acid is an aromatic dicarboxylic acid, more preferably one or more of terephthalic acid and isophthalic acid.

In a preferred embodiment, the ratio of ester bonds to carbonate bonds present in the copolyester carbonate resin is from 0.25 to 0.9 ester bonds per carbonate bond.

In a preferred embodiment, the copolyester-carbonate copolymer has a weight average molecular weight of from about 10,000 to about 200,000 g/mol.

Copolyester-carbonate resins are made by known methods, such as, for example, interfacial polymerization, transesterification, solution polymerization or melt polymerization.

Rubber modified thermoplastic resins suitable as the rubber modified thermoplastic resin of the present invention comprise a discontinuous elastomeric phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase and are known compounds whose preparation and properties have been described.

Suitable materials for use as the elastomeric phase are polymers those having a glass transition temperature (T_g) of less than or equal to 25°C, more preferably less than or equal to 0 °C, and even more preferably less than or equal to -30°C. As referred to herein, the T_g of a polymer is the T_g value of polymer as measured by differential scanning calorimetry (heating rate 20°C/minute, with the T_g value being determined at the inflection point).

In a preferred embodiment, the elastomer phase comprises a polymer having structural units derived from one or more monoethylenically unsaturated monomers selected from conjugated diene monomers, non-conjugated diene monomers or (C₁-C₁₂)alkyl(meth)acrylate monomers

Suitable conjugated diene monomers include, e.g., 1,3-butadiene, isoprene, 1,3-heptadiene, methyl-1,3-pentadiene, 2,3-dimethylbutadiene, 2-ethyl-1,3-pentadiene, 1,3-hexadiene, 2, 4, hexadiene,

dichlorobutadiene, bromobutadiene and dibromobutadiene as well as mixtures of conjugated diene monomers. In a preferred embodiment, the conjugated diene monomer is 1,3-butadiene.

Suitable non-conjugated diene monomers include, e.g., ethylidene norbornene, dicyclopentadiene, hexadiene or phenyl norbornene.

As used herein, the term "(C₁-C₁₂)alkyl" means a straight or branched alkyl substituent group having from 1 to 12 carbon atoms per group and includes, e.g., methyl, ethyl, n-butyl, sec-butyl, t-butyl, n-propyl, iso-propyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl, and the terminology "(meth)acrylate monomers" refers collectively to acrylate monomers and methacrylate monomers. Suitable (C₁-C₁₂)alkyl (meth)acrylate monomers include (C₁-C₁₂)alkyl acrylate monomers, e.g., ethyl acrylate, butyl acrylate, iso-pentyl acrylate, n-hexyl acrylate, 2-ethyl hexyl acrylate, and their (C₁-C₁₂)alkyl methacrylate analogs such as, e.g., methyl methacrylate, ethyl methacrylate, propyl methacrylate, iso-propyl methacrylate, butyl methacrylate, hexyl methacrylate, decyl methacrylate.

The elastomeric phase may, optionally, include up to about 40 percent by weight ("wt%") of one or more monomers selected from (C₂-C₈)olefin monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers.

As used herein, the term "(C₂-C₈)olefin monomers" means a compound having from 2 to 8 carbon atoms per molecule and having a single site of ethylenic unsaturation per molecule. Suitable (C₂-C₈)olefin monomers include, e.g., ethylene, propene, 1-butene, 1-pentene, heptene.

Suitable vinyl aromatic monomers include, e.g., styrene and substituted styrenes having one or more alkyl, alkoxy, hydroxyl or halo substituent group attached to the aromatic ring, including, e.g., α -methyl

styrene, p-methyl styrene, vinyl toluene, vinyl xylene, trimethyl styrene, butyl styrene, chlorostyrene, dichlorostyrene, bromostyrene, p-hydroxystyrene, methoxystyrene and vinyl-substituted condensed aromatic ring structures, such as, e.g., vinyl naphthalene, vinyl anthracene, as well as mixtures of vinyl aromatic monomers.

As used herein, the term "monoethylenically unsaturated nitrile monomer" means an acyclic compound that includes a single nitrile group and a single site of ethylenic unsaturation per molecule and includes, e.g., acrylonitrile, methacrylonitrile, α -chloro acrylonitrile.

The elastomeric phase may, optionally, include a minor amount, e.g., up to 5 wt%, of structural units derived from a polyethylenically unsaturated "crosslinking" monomer, e.g., butylene diacrylate, divinyl benzene, butene diol dimethacrylate, trimethylolpropane tri(meth)acrylate. As used herein, the term "polyethylenically unsaturated" means having two or more sites of ethylenic unsaturation per molecule.

The elastomeric phase may, particularly in those embodiments wherein the elastomeric phase has structural units derived from alkyl (meth)acrylate monomers, include a minor amount, e.g., up to 5 wt% of structural units derived from a polyethylenically unsaturated "graftlinking" monomer. Suitable graftlinking monomers include those monomers having a first site of ethylenic unsaturation with a reactivity similar to that of the monoethylenically unsaturated monomers from which the respective substrate or superstrate is derived and a second site of ethylenic unsaturation with a relative reactivity that is substantially different from that of the monoethylenically unsaturated monomers from which the elastomeric phase is derived so that the first site reacts during synthesis of the elastomeric phase and the second site is available for later reaction under different reaction conditions, e.g., during synthesis of

the rigid thermoplastic phase. Suitable graftlinking monomers include, e.g., allyl methacrylate, diallyl maleate, triallyl cyanurate.

In a preferred embodiment, the elastomeric phase comprises from 60 to 100 wt% structural units derived from one or more conjugated diene monomers and from 0 to 40 wt% structural units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers, such as, for example, a styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer or a styrene-butadiene-acrylonitrile copolymer.

In an alternative preferred embodiment, the elastomeric phase comprises structural units derived from one or more (C₁-C₁₂)alkyl acrylate monomers. In a more highly preferred embodiment, the rubbery polymeric substrate comprises from 40 to 95 wt% structural units derived from one or more (C₁-C₁₂)alkyl acrylate monomers, more preferably from one or more monomers selected from ethyl acrylate, butyl acrylate and n-hexyl acrylate.

In a preferred embodiment, the elastomeric phase is made by aqueous emulsion polymerization in the presence of a free radical initiator, e.g., an azonitrile initiator, an organic peroxide initiator, a persulfate initiator or a redox initiator system, and, optionally, in the presence of a chain transfer agent, e.g., an alkyl mercaptan and coagulated to form particles of elastomeric phase material. In a preferred embodiment, the emulsion polymerized particles of elastomeric phase material have a weight average particle size of 50 to 800 nm, more preferably, of from 100 to 500 nm, as measured by light transmission. The size of emulsion polymerized elastomeric particles may optionally be increased by mechanical or chemical agglomeration of the emulsion polymerized particles, according to known techniques.

The rigid thermoplastic resin phase comprises one or more thermoplastic polymers and exhibits a T_g of greater than 25°C, preferably greater than or equal to 90°C and even more preferably greater than or equal to 100°C.

In a preferred embodiment, the rigid thermoplastic phase comprises a polymer or a mixture of two or more polymers each having structural units derived from one or more monomers selected from the group consisting of (C₁-C₁₂)alkyl (meth)acrylate monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers. Suitable (C₁-C₁₂)alkyl (meth)acrylate monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers are those set forth above in the description of the elastomeric phase.

In a highly preferred embodiment, rigid thermoplastic phase comprises one or more vinyl aromatic polymers. Suitable vinyl aromatic polymers comprise at least 50 wt% structural units derived from one or more vinyl aromatic monomers.

In a preferred embodiment, the rigid thermoplastic resin phase comprises a vinyl aromatic polymer having first structural units derived from one or more vinyl aromatic monomers and having second structural units derived from one or more monoethylenically unsaturated nitrile monomers.

The rigid thermoplastic phase is made according to known processes, e.g., mass polymerization, emulsion polymerization, suspension polymerization or combinations thereof, wherein at least a portion of the rigid thermoplastic phase is chemically bonded, i.e., "grafted" to the elastomeric phase via reaction with unsaturated sites present in the elastomeric phase. The unsaturated sites in the elastomeric phase are provided, e.g., by residual unsaturated sites in

structural units derived from a conjugated diene or by residual unsaturated sites in structural units derived from a graftlinking monomer.

In a preferred embodiment, at least a portion of the rigid thermoplastic phase is made by an aqueous emulsion or aqueous suspension polymerization reaction in the presence of elastomeric phase and a polymerization initiator system, e.g., a thermal or redox initiator system.

In an alternative preferred embodiment, at least a portion of the thermoplastic phase is made by a mass polymerization process, wherein particles of the material from which the elastomeric phase is to be formed are dissolved in a solvent and added to a mixture of the monomers from which the rigid thermoplastic phase is to be formed and the monomers of the mixture are then polymerized to form the rubber modified thermoplastic resin.

The amount of grafting that takes place between the rigid thermoplastic phase and the elastomeric phase varies with the relative amount and composition of the elastomeric phase. In a preferred embodiment, from 10 to 90 wt%, preferably from 25 to 60 wt%, of the rigid thermoplastic phase is chemically grafted to the elastomeric phase and from 10 to 90 wt%, preferably from 40 to 75 wt% of the rigid thermoplastic phase remains "free, i.e., non-grafted.

The rigid thermoplastic phase of the rubber modified thermoplastic resin may be formed: (i) solely by polymerization carried out in the presence of the elastomeric phase or (ii) by addition of one or more separately polymerized rigid thermoplastic polymers to a rigid thermoplastic polymer that has been polymerized in the presence of the elastomeric phase. In a preferred embodiment, at least a portion of the rigid thermoplastic polymer is added as a separately polymerized rigid thermoplastic polymer.

In a preferred embodiment, the rubber modified thermoplastic resin comprises an elastomeric phase comprising a polymer having structural units derived from one or more conjugated diene monomers, and, optionally, further comprising structural units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers, and the rigid thermoplastic phase comprises a polymer having structural units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers.

Each of the polymers of the elastomeric phase and of the rigid thermoplastic resin phase of the rubber modified thermoplastic resin may, provided that the T_g limitation for the respective phase is satisfied, optionally include up to 10 wt% of third structural units derived from one or more other copolymerizable monomers such as, e.g., monoethylenically unsaturated carboxylic acids such as, e.g., acrylic acid, methacrylic acid, itaconic acid, hydroxy(C₁-C₁₂)alkyl (meth)acrylate monomers such as, e.g., hydroxyethyl methacrylate; (C₄-C₁₂)cycloalkyl (meth)acrylate monomers such as e.g., cyclohexyl methacrylate; (meth)acrylamide monomers such as e.g., acrylamide and methacrylamide; maleimide monomers such as, e.g., N-alkyl maleimides, N-aryl maleimides, maleic anhydride, vinyl esters such as, e.g., vinyl acetate and vinyl propionate. As used herein, the term "(C₄-C₁₂)cycloalkyl" means a cyclic alkyl substituent group having from 4 to 12 carbon atoms per group and the term "(meth)acrylamide" refers collectively to acrylamides and methacrylamides.

Particulate mineral fillers suitable for use as the mineral filler component of the composition of the present invention are known in the art and are available from a number of commercial sources and include, for example, alumina, barium carbonate, barium sulfate, barium titanate, barium trioxide, bismuth trioxide, calcium carbonate, magnesium silicate,

strontium ferrite, titanium dioxide, wollastonite, zinc oxide and mixtures thereof.

In a preferred embodiment, the mineral filler of the composition of the present invention comprises wollastonite, magnesium silicate, that is, talc, or mixture thereof.

Suitable particles are those having mean largest characteristic dimension of from 0.1 micrometer ("μm") to 30 μm, more preferably from 0.5 μm to 20 μm and even more preferably from 1.5 μm to 5 μm. As used herein the terminology "largest characteristic dimension" means the greatest dimension exhibited by the particles along any one dimension. As used herein, the mean greatest characteristic dimension of an elongated particle, such as, for example, a fiber or rod-shaped particle, would correspond to the mean length of the particles and the mean greatest characteristic dimension of, for example, a flat or spherical particle or a particle having a platelet morphology, would be its mean particle size as measured by a sieve analysis. As used herein, the terminology "mean particle size" means the corresponding size of meshes in a sieve through which 50 wt% of the dry particles will pass and 50 wt% are withheld.

In a preferred embodiment, the particles exhibit an aspect ratio of from greater than 1 to 30, more preferably from 2 to 15, wherein the terminology aspect ratio as used herein means the ratio of the greatest characteristic dimension of the particle to the next greatest characteristic dimension of the particle. For example, the aspect ratio of an elongated fiber would be the ratio of the length of the fiber to its diameter, and the aspect ratio of a platelet would be the ratio of the width or diameter of the platelet to its thickness.

Other Additives

The thermoplastic resin composition of the present invention may optionally also contain various conventional additives, such as

antioxidants, stabilizers, flame retardant compounds, UV absorbers and light stabilizers, other fillers and reinforcing agents in addition to the particulate mineral fillers disclosed above, as well as lubricants, plasticizers, optical brighteners, pigments, dyes, colorants, anti-static agents and blowing agents.

The thermoplastic resin composition of the present invention is made by combining and mixing the components of the composition of the present invention under conditions suitable for the formation of a blend of the components, such as for example, by melt mixing using, for example, a two-roll mill, a Banbury mixer or a single screw or twin-screw extruder, and, optionally, then reducing the composition so formed to particulate form, e.g., by pelletizing or grinding the composition.

The thermoplastic resin composition of the present invention can be molded into useful shaped articles by a variety of means such as injection molding, extrusion, rotational molding, blow molding and thermoforming to form articles such as, for example, automotive exterior door panels, tailgates or trim components.

Example 1

A blend containing 52 part per hundred ("pph") of high molecular weight polycarbonate having a weight average molecular weight ("Mw") of about 55,000 g/mol, 22.5 pph low molecular weight polycarbonate having an Mw of about 45,000 g/mol, 7.75 parts of solution polymerized butadiene rubber post-grafted with polystyrene, 9.40 pph of a high-flow styrene-acrylonitrile copolymer having a Mw of about 65, g/mol, 0.25 pph of pentaerythritol tetrastearate, 0.5 pph of thermal stabilizer of pentaerythritol beta lauryl thiopropionate and octyl decyl (3,5 di-t-4 hydroxyhydro) cinnamate, 0.15 pph of bis (2,4 di-t-butyl phenyl) pentaerythritol diphosphite, 0.50 parts carbon black, and 8.0 pph of different talcs sizes as set forth in TABLE 1. The components of the blend were mixed in a Henschel type blending device and

extruded using a Werner and Pfl iderer 30 millimeter ("mm") twin screw extruder. Barrel temperatures were set to provide a melt temperature at the die of approximately 520°F. The screw was run at 400 revolutions per minute ("rpm"), and a vacuum vent was used at 28 inches of mercury. Strands were cooled in a water bath and then pelletized using a rotating knife device. Each composition was prepared as described above. The results of the tests are listed in TABLE I and were the average of five samples each.

TABLE 1

| | MVI | HDT | Notched Izod | | |
|------------|---------|---------|--------------------|-----------------------|-------|
| | @ 260°F | @66 psi | <u>Ft-Lb./Inch</u> | <u>Dynatup Ft-Lb.</u> | |
| | w/5Kg. | °F | RT | - RT | - |
| | | | 30°C | 30°C | |
| Microtalc* | 11.45 | 272.1 | 3.59 | 2.15 | 41.88 |
| MP-25-38 | | | | | 39.12 |
| Microtalc* | 11.01 | 272.8 | 4.31 | 2.30 | 45.18 |
| MP-12-50 | | | | | 40.70 |
| Ultratalc* | 10.62 | 272.7 | 7.22 | 2.33 | 46.28 |
| 609 | | | | | 42.13 |

*Barretts Minerals Inc., Dillon, Montana

MVI - melt volume Index determined in accordance with ASTM D-1238.

HDT - heat distortion temperature under load determined in accordance with ASTM D-648.

MP-25-38 - talc having a bulk density of about 12.0 pounds/ft³, a Hegman fineness of about 5.75 and a median particle size of 2.4 µm.

MP-12-50 - talc having a bulk density of about 7.5 lb./ft³, a Hegman fineness of about 6.0. and a median particle size of 1.2 µm.

Ultratalc 609 - talc having a bulk density of about 6 lbs/ft³, a Hegman fineness of about 7 and a mean particle size of 0.6 µm.

RT - room temperature.

For the Notched IZOD impact test, the test specimens were about 3 1/2 inches wide by 1/8 inch thick and were tested in accordance with ASTM D756.

The Dynatup test was performed under ASTM test procedure D3763-86 using the Dynatup impact testing equipment by General Research Instruments. Briefly, the test procedure involves subjecting samples to a

falling dart impact. The dart is about a 0.5 inch diameter rod about 1/5 inch long and had a rounded, blunt end, which is the end that impacts upon the sample. The molded sample of about 4 inch in diameter by about 1/8 inch thick is clamped in a holding device. The dart is on the vertical sled and shaft, with weights added for energy impact determination. The test is designed to force failure of the sample in order to determine the type of failure occurring. The average velocity of the falling dart was about 11.3 feet per second, and the impact energy was 100 foot-pounds, with a drop height of two feet. In the Dynatup impact, the energy absorbed by the sample by the falling dart is plotted on a graph from the time the dart first hits the sample until it punctures through the sample. E(tot) is the total energy absorbed over the range of time the dart first hits the sample until it punctures through the sample.

Example 2

Photomicrographs were also taken of a molded sample containing Microtalc MP-25-38 talc of Example 1. The photomicrographs show that the talc particles are encapsulated in free styrene-acrylonitrile (SAN), and further show the encapsulated particles and rubber particles are dispersed in the polycarbonate phase. The photomicrographs are attached as FIG. 1 and FIG.2.

Example 3

Example 1 was repeated except that 74.5 pph of a polycarbonate having a Mw of about 55,000 g/mol was employed herein in place of the two (2) polycarbonate components of Example 1. The results obtained were as follows and are the average of five samples each:

TABLE 2

| | MVI | HDT | Notched Izod | | |
|------------|---------|---------|--------------------|-----------------------|-------|
| | @ 260°F | @66 psi | <u>Ft-Lb./Inch</u> | <u>Dynatup Ft-Lb.</u> | |
| | w/5Kg. | F | RT | - RT | - |
| | | | 30°C | 30°C | |
| Microtalc* | 11.86 | 272.1 | 3.76 | 2.14 | 43.24 |
| MP-25-38 | | | | | 40.58 |
| Microtalc* | 10.89 | 272.5 | 5.47 | 2.30 | 43.52 |
| MP-12-50 | | | | | 42.03 |
| Ultratalc* | 10.68 | 272.1 | 8.75 | 2.45 | 46.56 |
| 609 | | | | | 44.58 |

All definitions are the same as TABLE 1.

Example 4

Example 1 was repeated except that the formulations employed herein are set forth in TABLE 2 was employed herein and the inorganic mineral additive was wollastonite having an average mean diameter of less than 4.5 μm and an average length of about 24 μm .

The results of the tests are listed in TABLE 3

TABLE 3.

| Ingredients | | Formulation | |
|---------------------|---|-------------|-------|
| PC-1 | 62.0 | | 30 |
| PC-2 | | | 32 |
| PC-3 | | 62.0 | |
| HRG | 13.5 | 13.5 | 13.5 |
| SAN | 16.5 | 16.5 | 16.5 |
| Wollastinite | 8.0 | 5.0 | 8.0 |
| Ultratalc 609 | | 3.0 | |
| (same as Example 1) | | | |
| PETS | 0.5 | 0.5 | 0.5 |
| Irganox | 0.20 | 0.2 | 0.2 |
| Carbon Block | 0.5 | 0.5 | |
| HDT | 259°F | 263°F | 226°F |
| Notched IZOD | | | |
| Ft.-Lb./Inch | | | |
| RT | 10.6 | 10.7 | 7.5 |
| -20°F | 2.2 | 2.2 | 2.0 |
| Dynatup | | | |
| RT E(tot) | 39.6 | 38.6 | 40.7 |
| -20°C E(tot) | 35.3 | 33.9 | 35 |
| PC-1 | Polycarbonate resin having an Mw of about 50,000 g/mol. | | |
| PC-2 | Polycarbonate resin having an Mw of about 35,000 g/mol. | | |
| PC-3 | Polycarbonate resin having an Mw of about 45,000 g/mol. | | |
| HRG | Styrene/butadiene high rubber graft. | | |
| SAN | Mw of about 60,000 - 70,000 g/mol. | | |
| PETS | Pentaerythritol tetrastearate. | | |
| Irganox | Octyl decyl (3,5 di-t-butyl 4 hydroxyhydro) cinnamate. | | |
| HDT | Heat Distortion Temperature ASTM D-648. | | |

All other definitions are the same as in TABLE 1.

Example 5

The components of the blend of Example 1 above (exclusive of the high molecular weight polycarbonate) were mixed with a Mixaco high-intensity type blending device. The mixture was fed to the extruder separately from the high molecular weight polycarbonate. In this case Werner and Pfleiderer 58 mm twin screw extruder was used. Barrel temperatures were set to provide a melt temperature at the die of approximately 580°F. The screw was run at 400 rpm, and a vacuum vent was used at 28 inches of mercury. Total output was approximately 900 pounds per hour. Strands were cooled in a water bath and then pelletized using a rotating knife device. The formulation was designated as Inventive Formulation 1.

To determine the degree of dimensional stability of the formulation of this invention, five panels of about 4 pounds each were injection molded. The panels were molded at an injection molding temperature of about 580°F and a molding cycle of about 90 seconds.

When the panels cooled to room temperature, the panels were measured from corner to corner across the panel's largest dimension for a base reference dimension number. The panels were then coated with a primer, followed by a pigmented coating and then a clear coat. The painted panels were placed in an oven set at 240°F. However, it was noticed that the oven temperature went to 260°F before cycling to the control temperature of 240°F. The panels were removed from the oven and again measured from corner to corner as previously measured prior to exposure to the heat phase of the oven in order to determine the change in dimension with respect to the reference dimension. The average result obtained was an average of the panels and was as follows:

Invention Formulation 1

0.3 mm difference

Example 6

This Example 6 is set forth to determine the sag characteristics of the composition of the formulation of this invention. Invention Formulation 1 of Example 5 was molded into five panels under the same conditions as Example 5. The panels were put into a frame and each panel was measured while in a horizontal position at about 36 points to obtain an average reference dimension in order to determine sag vertically or change from the horizontal measurement after exposure to a bake oven.

Each molded panel was painted as in Example 4 and each placed in an oven at a temperature of 240°F, 258°F, 266°F and 275°F respectively. Each panel after cooling to room temperature was measured in a horizontal position at essentially the same 36 points on the panel. The difference in measurement prior to and after exposure to the heat oven was a determination of sag or depression. The average of all points of measurement of the 5 panels was as follows:

| | <u>240°F</u> | <u>258°F</u> | <u>266°F</u> | <u>275°F</u> |
|-------------------------|--------------|--------------|--------------|--------------|
| Invention Formulation 1 | -0.4 mm | -0.65 mm | -0.75 mm | -1.1 mm |

The minus is the drop or sag difference in the panel dimension prior to and after oven exposure.

Example 7

Two compositions were prepared in accordance with Example 1, namely one composition contained Microtalc MP-25-38 and the second composition contained, instead of the Microtalc MP-25-38, the wollastonite of Example 4.

The compositions were injection molded into test bars at a temperature of about 580°F. The test bars were prepared and tested for sag resistance in accordance with ASTM D-3769. The samples were individually exposed to the temperatures set forth in TABLE 3 respectively. The results obtained are reported in TABLE 4 below.

TABLE 4

| | 230°F | 240°F | 250°F | 260°F | 270°F | 280°F |
|----------------|-------|--------|--------|--------|--------|-------|
| Microtalc | <1.0 | <1.0 | 3.5 | 4.5 | 5.2 | 8.0 |
| MP-25-38 | | | | | | |
| Wollastonite | 3.0mm | 3.0 mm | 5.5 mm | 6.8 mm | 9.8 mm | 16.7 |
| mm | | | | | | |
| Comparative | 3.0 | 5.0 | 5.5 | 8.3 | 12.0 | 20.5 |
| Formulation 1* | | | | | | |

*Pulse™ B250 filled Polycarbonate/ABS resin blend sold by The Dow Chemical Company.

The composition of the present invention exhibits unexpectedly improved dimensional stability, improved thermal stability, improved impact resistance, particularly at low temperatures, and improved flow properties.

CLAIMS:

1. A thermoplastic resin composition, comprising, based on 100 parts by weight of the composition:

- (a) from 65 to 85 parts by weight of one or more aromatic polycarbonate resins,
- (b) from 10 to 50 parts by weight of a rubber modified graft copolymer, comprising a discontinuous elastomeric phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase, and
- (c) from 1 to 15 parts by weight of a particulate mineral filler having a mean largest characteristic dimension of from 0.1 micrometer to 30 micrometers.

2. The composition of claim 1, wherein the composition comprises, based on 100 parts by weight of the composition, from 70 to 80 parts by weight of the aromatic polycarbonate resin, from 10 to 24 parts by weight of the rubber modified graft copolymer, from 6 to 10 parts by weight of the talc.

3. The composition of claim 1, wherein the aromatic polycarbonate resin comprises one or more linear aromatic polycarbonate resins, each derived from bisphenol A and phosgene and each having a respective weight average molecular weight of from about 10,000 to about 200,000 grams per mole.

4. The composition of claim 1, wherein the rubber modified thermoplastic resin comprises an elastomeric phase comprising structural units derived from one or more conjugated diene monomers and a rigid thermoplastic phase comprising structural units derived from one or more

monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers.

5. The composition of claim 1, wherein the particulate mineral filler is selected from wollastonite, talc and mixtures thereof.

6. The composition of claim 1, wherein the mean greatest characteristic dimension of the particulate mineral filler is from 0.5 micrometers to 20 μm micrometers.

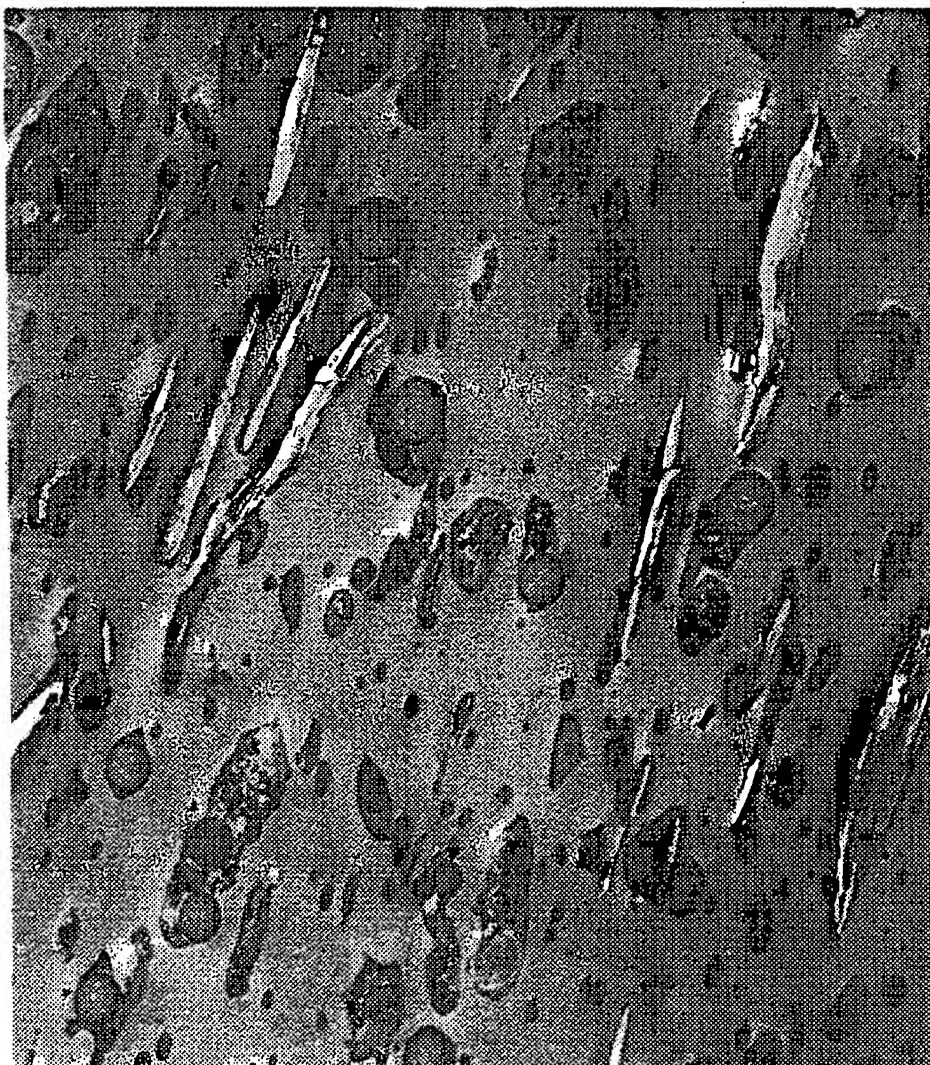
7. The composition of claim 1, wherein the mean greatest characteristic dimension of the particulate mineral filler is from 1.5 micrometers to 5 micrometers.

8. The composition of claim 1, wherein the particulate mineral filler exhibits an aspect ratio of from greater than 1 to 30,

9. The composition of claim 1, wherein the particulate mineral filler exhibits an aspect ratio of from 2 to 15.

10. An article molded from the composition of claim 1.

1 / 2



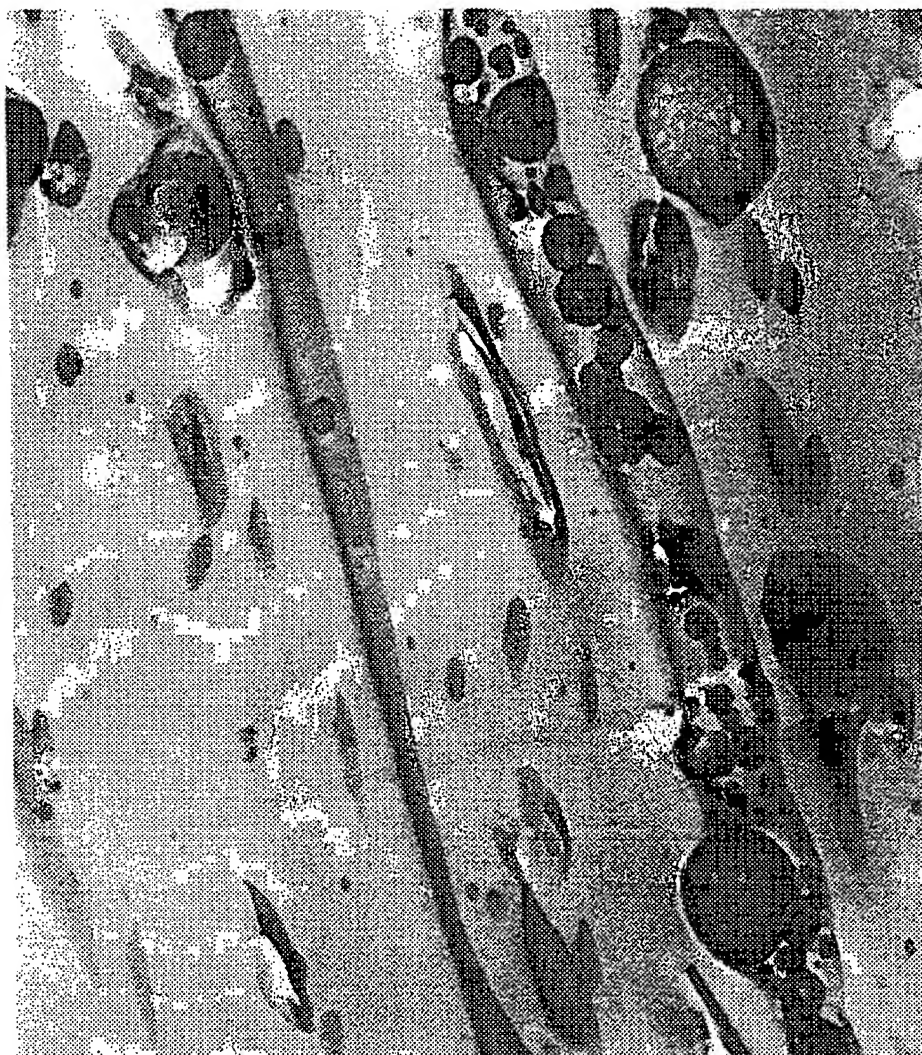
Os, Ru 45 Sec

20 kx

MC 8800 BLEND 1
MELT TEMPERATURE HIGH, POSITION 3

FIG. 1

SUBSTITUTE SHEET (RULE 26)



Os, Ru 45 Sec

60 kx

MC 8800 BLEND 1
MELT TEMPERATURE HIGH, POSITION 7

FIG. 2

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/09950

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K3/34 C08L69/00 C08L51/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 5 091 461 A (SKOCHDOPOLE RICHARD E) 25 February 1992 see claims 1,4-9; examples RUN,5-13 | 1-10 |
| Y | --- | 5 |
| A | EP 0 135 904 A (MOBAY CHEMICAL CORP) 3 April 1985 see page 5, line 20 - page 7, line 45; claims 1-4; examples 1-7 | 1-10 |
| X | US 5 162 419 A (POTTIER-METZ CATHERINE M M ET AL) 10 November 1992 cited in the application see claims 1-20; example EXAMPLES | 1-7,10 |
| Y | US 4 937 287 A (AMOCO CORPORATION) 26 June 1990 see column 16, line 50-55 | 5 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/09950

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| US 5091461 A | 25-02-1992 | AU 630180 B AU 5298690 A CA 2014012 A DE 69029338 D DE 69029338 T EP 0391413 A JP 2294358 A JP 7033473 B MX 165089 B | 22-10-1992 11-10-1990 07-10-1990 23-01-1997 05-06-1997 10-10-1990 05-12-1990 12-04-1995 21-10-1992 |
| EP 0135904 A | 03-04-1985 | JP 60092350 A | 23-05-1985 |
| US 5162419 A | 10-11-1992 | FR 2661184 A CA 2037743 A DE 69114892 D DE 69114892 T EP 0452788 A ES 2081382 T JP 2666003 B JP 4227650 A MX 174337 B | 25-10-1991 20-10-1991 11-01-1996 01-08-1996 23-10-1991 01-03-1996 22-10-1997 17-08-1992 09-05-1994 |
| US 4937287 A | 26-06-1990 | CA 1317695 A EP 0331312 A JP 2004836 A | 11-05-1993 06-09-1989 09-01-1990 |